Force induced triple point for interacting polymers

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We show the existence of a force induced triple point in an interacting polymer problem that allows two zero-force thermal phase transitions. The phase diagrams for three different models of mutually attracting but self avoiding polymers are presented. One of these models has an intermediate phase and it shows a triple point but not the others. A general phase diagram with multicritical points in an extended parameter space is also discussed.

Soon after the discovery of the double helical structure of double stranded DNA (dsDNA), its melting by change of temperature or the pH of the solvent was recognized[1]. Only recently it has been realized that there can be a force-induced unzipping transition[2] of a DNA with a force applied solely at one end. In both the thermal and the forced cases, the phase transition takes a double stranded form to two single strands. The prediction of the unzipping transition based on interacting Gaussian chains[2] was immediately reconfirmed by a dynamical approach[3]. Results on the unzipping transition are now available from extensive exact solutions of lattice models[4, 5, 6], simple models of quenched-averaged DNA [7], Monte Carlo simulations of a three dimensional model with self- and mutually-avoiding walks [8] etc., on the theoretical front, and for real DNA from experiments[9]. From the theoretical results, it emerges that the qualitative features of the unzipping transition are insensitive to the dimensionality (d) of the models and are seen even in two dimensional models. These results include a re-entrance[4, 5, 6] in the low temperature region.

In the systems studied so far, there is only one zero force thermal phase transition. In such cases, with two intensive variables, temperature T and force g, there is an unzipping transition line, $g = g_c(T)$, in the $g - T$ plane, demarcating the bound or zipped phase from the unzipped phase. This gives the unzipping phase boundary. In case there are more than one transition, the phase diagram will be influenced by the intermediate phases. Our aim is to determine such a global phase diagram for the unzipping transition where the existence of an intermediate phase leads to a triple point in the $g - T$ plane.

We introduce three models, A, B and C, which differ in the nature of the mutual interaction of the two strands. These models are general enough to be defined in any d though, for computational limitations, we consider the two dimensional square lattice version only. Let us consider two linear polymer chains which are mutually-attracting-self-avoiding [10] in nature. On a square lattice, the polymers are not allowed to cross each other as shown in Fig. 1. Monomers are the sites
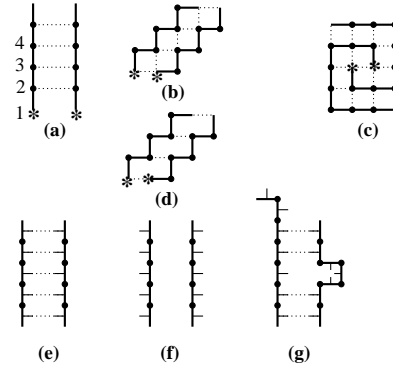

FIG. 1: Figures (a-d) represent the possible conformations of models A and B. In model A any monomer of one strand can interact with any monomer of the other strand. (a) and (b) are two possible states with (c) representing a possible ground state. For model B, the ith monomer of one strand interacts with the ith monomer of the other strand. In this case (a) represents the ground state, (d) represents a partial bound state. Note that (d) differs from (b) in the nature of interactions represented by the dotted lines. In model B, (c) has no valid interaction and would represent an open state. Figures (e,f,g) represent model C where bases are on the links of the strands with short stubs representing orientation. (e) the completely zipped state, (f) a non pairing configuration, and (g) a partial bound configuration. In all cases dotted lines show the attractive interactions.

occupied by the polymers and the interactions are among the "bases" (defined next) so that an interacting pair may also be called a base pair. In models A and B, the bases are the monomers while in C the bases are associated with the links. We allow an attractive interaction between monomers or bases only if they are of opposite strands and are nearest neighbours on the lattice. The nearest neighbour interaction mimics the short range nature of the hydrogen bonds. In model A, any monomer of one strand can interact with any monomer of the other strand. In model B, monomer i of one strand can interact only with the ith monomer of the other strand. This model is similar to the models of DNA studied earlier[11]. In model C, we associate the bases with the bonds of
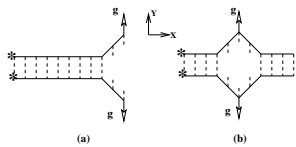
FIG. 2: Schematic figures for a force (a) applied at one end, and (b) applied at the middle. Fixed end points are indicated by stars.

FIG. 3: Variations in fluctuation of m with temperature (T) for $g = 0.0$ and 0.1 are shown for model A (a) and model B (b). In model B and C we do not find two peaks. The first peak in (a) corresponds to a transition where spiral conformation goes over to a zipped conformation. The second peak in (a) and the peak in (b) correspond to the unzipping transition.

the strands. In one strand the bases point towards the right while on the other they are on the left, as one traverses the chains sequentially[12]. Pairing between complimentary strands takes place only when the bases approach each other directly without the strands coming in-between, as shown in Fig. 1). Such a model has been studied recently in the context of relative stabilities of DNA hairpin structures[13]. The figure also shows a situation where pairing cannot take place and such configurations are counted in the unbound states. The interactions are shown by dotted lines in Fig. 1). The interaction energy in all the cases is taken as $-\epsilon(\epsilon > 0)$ and we shall choose $\epsilon = 1$. In all cases the monomers at one end (index=1) of each strand are always kept fixed occupying nearest neighbour sites on the lattice.

For model A the ground state is a spiral of the type shown in Fig. 1c while for model B and C it is a zipped state as in Fig. 1a,e. Because of the constraint of holding the monomers with index 1 at nearest neighbour sites, model A is also equivalent to a diblock copolymer model[14] which has two phase transitions in zero force with increasing temperature. The polymers go from a compact spiral-like phase to a zipped phase which then melts at a still higher temperature. It is this intermediate phase that is of interest to us. In view of the simple ground state in models B and C, no such intermediate phases are expected or known.

A force is applied at one end (Fig.2(a)) or at the middle (Fig. 2(b)) of the chains, in the y-direction. The contribution to energy by this force is $-gy$ where y is the absolute distance in the y-direction between the two strands at the point of application of the force. A recent study[6] showed a rich phase diagram when a force is applied somewhere in the interior. Furthermore, such situations occur in many processes like gene-expression where RNA is formed in bubbles or eye-type configurations on DNA. Motivated by these, we consider the case of a force applied at the mid point. A low temperature analysis shows that the phase diagram is expected to be different from the end case. We compare the $g - T$ phase diagrams of model A vs models B and C.

The thermodynamic properties associated with the unzipping transition are obtained from the partition function which can be written as a sum over all possible con-
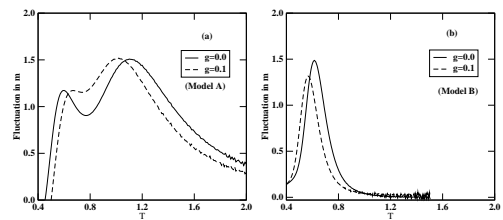
figurations

$$Z_N(\omega, u) \;=\; \sum_{m,y} C(m,y)\omega^m u^y. \tag{1}$$

Here N is the chain length of each of the two strands, $\omega = \exp(1/T)$ is the Boltzmann weight associated with each base pair (taking the Boltzmann constant $k_B = 1$) and m is the total number of intact base pairs in the chain. Finally u is the Boltzmann weight, $\exp(g/T)$ associated with force. $C(m,y)$ is the number of distinct configurations having m base pairs whose end (or mid) points are at a distance y apart. We have obtained $C(m,y)$ for $N \leq 16$ monomers in two dimension ($d = 2$) and analyzed the partition function through series analysis. We prefer this technique because in this case the scaling corrections are correctly taken into account by suitable extrapolation technique. To achieve the same accuracy by the Monte-Carlo method, a chain of about two orders of magnitude larger than in the exact enumeration method has to be considered [15].

The reduced free energy per base pair is found from the relation

$$G(\omega, u) = \lim_{N \to \infty} \frac{1}{N} \log Z(\omega, u). \tag{2}$$

The limit $N \to \infty$ is found by using the ratio method [16] for extrapolation. The transition point for zero force (i.e. thermal melting) can be obtained from the plot of $G(\omega, u)$ versus ω or from the peak value of $\partial^2 G / \partial (\ln \omega)^2$. For self-avoiding walk at $u = 1$, we find $T_c = 1.1 \pm 0.1, 0.61 \pm 0.08, 0.59 \pm 0.08$ for models A, B and C respectively. With a force ($u \neq 1$), the phase boundary is obtained from the fluctuation in m. Fig. 3 shows the variation of fluctuation of m with temperature for model A and B.

The phase diagrams are shown in Fig. 4.

The phase diagram for Model A has several distinctive features. We see two peaks in the temperature dependence of the fluctuation in m for small g. At low T there is a spiral structure with vanishing entropy but as T increases ($T > 0.5$) the chains acquire a zipped state,
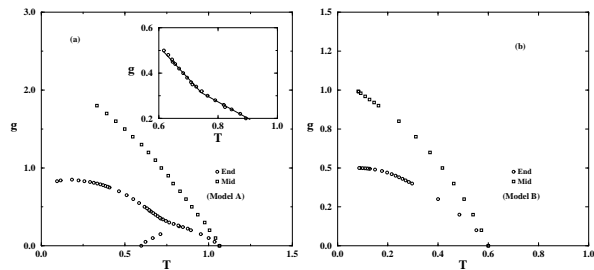
FIG. 4: Force-Temperature (g-T) phase diagrams for the end and the mid case. (a) for model A, (b) model B and model C within errorbar.

FIG. 5: Possible phase diagrams *without any triple point* in the $g-T$ plane. Phase 2 (a) may persist till $T = 0$ under force, (b) may persist under force but disappears at $T = 0$, or (c) exists only over a limited range of force and temperature. In (a) the sequence of 1-2-unzipped transitions will be observable in the groundstate itself, while in (c) a reentrant behaviour will be observable within phase 1 itself.

eventually unzipping at higher temperatures. The low temperature peak is the transition where the spiral state goes over to the zipped state while the second peak is the unzipping transition. Although model C is a more realistic model for representation of dsDNA, we find the phase diagram to be almost the same as that of model B. This may be taken as an ıa posteriori justification of using model B for DNA. (However, in case of hetrogeneous chains, model C may give intermediate states by forming the hairpin kind of structure as shown in Fig1 e. Such structures are not possible in model B.)

Our results are based on the $N = 16$ (32 monomers) enumerations. For this length there is significant surface contribution. The ground state energy is $E_0 = -(2N - O(\sqrt{N}))$ while the ground state energy is $E_0 = -N\epsilon$ for both models B and C for a DNA with N monomers or bases each. The $O(\sqrt{N})$ correction for model A comes from the monomers on the boundary. If we ignore the surface contribution (valid for large N) the spiral to zipped state transition temperature T_{c1} may be estimated from a simple energy balance argument. The spiral state has an energy $E_0 = -2N$ with negligible entropy while the zipped state has the free energy $= -N - NT \ln \mu_b$, where $\ln \mu_b$ is the entropy per base pair of the zipped phase. Equating these two we get

$$T_{c1} = 1/\ln \mu_b - O(N^{-1/2}), \tag{3}$$

where the surface correction has also been shown. If we use $\mu_b = 2.682$, the connectivity constant for the square lattice self-avoiding walk[10], we find $T_{c1} \approx 1.04$ which is close to the value known from other estimates[14]. Since the surface correction lowers the estimate of T_{c1}, our value of $T_{c1} = 0.5$ is consistent with the form of Eq. 3.

The surface contribution ($O(\sqrt{N})$ in the spiral state for small chains is not negligible, and it helps in the stabilization of of the spiral structure over the zipped phase for small g because of the extra energy $\sim g\sqrt{N}$. As a result, the phase boundary obtained has a finite slope. For large N, the force term should not affect the spiral to zipped transition since the force affects the relative separation of the strands. Therefore one would expect
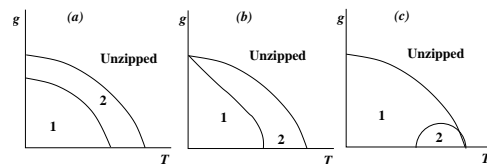
a phase boundary parallel to the g-axis *meeting the unzipping phase boundary at a triple point*. Other possible phase diagrams are shown in Fig. 5. From thermodynamic stability analysis[17], it is known that the angle between two coexistence lines at a triple point in a phase diagram has to be less than π. Therefore, a discontinuity in the slope in the unzipping phase boundary in the $g-T$ plane is expected at the potential triple point. The inset in Fig. 4a shows the meeting of the two unzipping boundaries. Our main result is the prediction of the coexistence of all the three phases in the $g-T$ phase diagram for model A - a phenomenon not possible without force.

At $T = 0$, the critical force can be found from a matching of the ground state energy with the energy of the completely unzipped state. If the force stretches the strands completely, the unzipped state has the energy $= -2Ng$ taking the bond length to be unity. Comparing this with the bound state energy E_0, we see $g_c(T = 0) = E_0/2N$. For large N, $E_0 = 2N$ and so we get $g_c(T = 0) = 1$, while it is 0.5 for models B and C. For finite N, if the surface correction is taken into account, then $g_c = 1 - (1/\sqrt{2N}) \approx 0.8232$ for $N = 16$. The value shown in Fig. 4 is very close to this estimate rather than the large N value. Any extrapolation therefore would have to take into account this surface correction properly. In absence of any large N data we do not attempt such extrapolations here for model A.

The low temperature phase boundary for the mid case can be obtained by an extension of the $T = 0$ argument given above. Following Ref. [6], let us consider the situation with the force applied at a position sN, $(0 < s \leq 1)$, from the fixed end. The unzipped state has the energy $= -2sNg$ taking the bond length to be unity. Comparing this with the bound state energy we see $g_c(T = 0) = a/2s$ where $a = 2$ for model A but $a = 1$ for models B and C. We see a factor of 2 difference in the end vs mid case.

Close to $T = 0$, the free energy of a bubble of $2m$ base pairs with respect to the completely bound state is

$$\Delta F = 2m(a + T \ln \mu_b) - gm, \tag{4}$$

where $\ln \mu_b$ is the entropy per base pair of the bound state which is lost on unzipping m pairs. For the mid case a
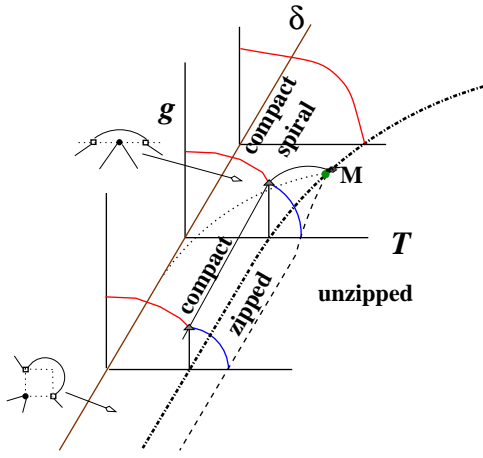
FIG. 6: Proposed phase diagram in $g - T - \delta$ space. M is the multicritical point (at zero force) where the zipped phase vanishes as δ is made negative (attractive three-body interaction). The dotted line in the $g = 0$ plane is a crossover line for a δ-interaction dominated phase to go over a non-spiral compact phase dominated by interactions at corners. The triangular region in the $g - T$ plane for the zipped phase vanishes at M. M is therefore the end point of the line of triple points (thin line through the triangles).

large m is favourable ($m \leq N/2$) if $g > g_c(T) \equiv 2(a + T \ln \mu_b)$. In case $\ln \mu_b > 0$, we see a positive slope and hence a re-entrance, in the low temperature region. In all the three models studied here, $\ln \mu_b = 0$, and therefore no re-entrance.

The results for model A can be extended to a case with a three body interaction that stabilizes the spiral phase[14]. Let there be an interaction δ that favours a configuration with a monomer of one strand sandwiched between the monomers of the other strand on the two nearest neighbors on the same axis. Let us call such contact as δ-contact. For $\delta < 0$ (i.e. attractive three body interaction) the compact spiral phase is the ground state as at $\delta = 0$. For large negative δ, there is only one denaturation transition. Therefore a multicritical point occurs in the $g = 0(\delta - T)$ plane. This is indicated by M in Fig. 6. For repulsion, $\delta > 0$, one may have a compact ground state without any δ-contact. In this case the ground state need not be a spiral and will have a mixture of double contacts (e.g. at corners) and single contacts. Let these occur in proportion $p : (1-p)$ ($p < 1$). The ground state energy is then $-N(1+p)$. A meanfield estimate of equal proportion gives $E = -(3/2)N$. This energy needs to be compared with the energy of the spiral state, namely $-2N + 2N\delta$ for $N \rightarrow \infty$. At $T = 0$, a change in the ground state structure occurs at $\delta = 1 - p \approx 0.5$. In the $\delta - T$ phase diagram one will have a crossover line (dotted line in Fig. 6) which should end in the $\delta - T$ plane at the multicritical point which is the confluence of the two zero-force thermal transitions. For large negative δ, the compact phase goes over directly

to the unzipped phase and therefore no triple point can exist on the unzipping boundary. The $g - T - \delta$ phase diagram is schematically shown in FIg. 6.

To summarize, we have shown in this paper the existence of a force induced triple point in a problem of interacting polymers where the interactions allow an entropy-stabilized phase before melting. This opens up the possibility of much richer phase transitions and other multi-critical behaviours in polymeric systems when subjected to force. We hope that single molecule experiments would be able to explore experimentally this new area in polymers.

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